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Nano-Zeolite Amendment to Minimize Greenhouse Gas Emission in Rice Soil

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Abstract

A greenhouse study was undertaken to determine nitrogen dynamics and greenhouse gas (GHG) emissions in rice soils amended with nano-zeolite based nitrogenous fertilizer application. It is hypothesised that nano-fertilizer carrying N regulates the release of N in rice soils that minimizes greenhouse gas emission while improving the availability of N in judicious combination. Nano-fertilizer carrying NO_3^- or NH_4^+ forms of nitrogen were synthesized using commercial nano-zeolite by fortifying two forms of N. The nano-zeolite was characterized before and after loading N. Nitrogen release pattern of synthesized nano-fertilizers (nitrate and ammonical forms) was studied in a percolation reactor. The data have shown that N release from the nano-fertilizer (NH4+ form) and conventional fertilizer (ammonium sulphate) were 480 and 310hrs, respectively. On the other hand, the N release from nano-fertilizer (NO_3^- form) and conventional (potassium nitrate) were 280 and 210 hrs, respectively. This suggests that both forms of nano-fertilizer release N slowly and steadily for an extended period of time. Soil fertilized with nano-fertilizer (NH_4^+ - N) recorded lower N_2O emission (1.8 mg m^{-2} day^{-1}) than conventional fertilizer (2.7 mg m^{-2} day^{-1}). On the other hand, soil fertilized with nano-fertilizer (NO_3^- - N) registered lower CH_4 flux (34.8 mg m^{-2} day^{-1}) than conventional fertilizer (36.8 mg m^{-2} day^{-1}). These data suggest that the nano-fertilizer regulates the release of N that closely coincided with the benefit of reduction in GHG emission.

Keywords: *Ammonium Sulphate; Methane; Nano-fertilizer; Nitrous oxide Zeolite.*

1. INTRODUCTION

Nitrogen is "kingpin" in plant nutrient kingdom often deficient in tropical soils due to faster decomposition of organic matter. It has been estimated that more than 95% of Indian soils are found deficient and need for continuous application to sustain farm productivity Taraftar (2016). Despite the importance N application is unequivocally demonstrated, N use efficiency by crops hardly exceeds 30-35% due to the wastages of added N caused by leaching, volatilization and immobilization (Olk, 1999). In order to improve N use efficiency, several slow / controlled release fertilizers such as coated urea with neem, tar coated, gypsum and polymers were introduced and discontinued due the non-availability or expensive. With a view to improve N use efficiency, nano-fertilizers have been investigated with a view to extend the release of N for an extended period of time which closely coincided with the release of greenhouse gas emission.

Nano-fertilizers are nutrient carriers of nano-dimensions ranging from 30-40 nm (10^{-9} m or one-billionth of a meter) and capable of holding bountiful of nutrient ions due to their high surface area and release it slowly and steadily that commensurate with crop demand. Sharmila Rahale (2011) has monitored the nutrient release pattern of nano-fertilizer formulations carrying fertilizer nitrogen. The data have shown that the nano-clay-based fertilizer formulations (zeolite and montmorillonite with a dimension of 30–40 nm) are capable of releasing the nutrients particularly N for a longer period of time (>1,000 h) than conventional fertilizers (<500 h). Further, Manikandan and Subramanian (2014) reported that the ball milling of zeolite at 1, 2, 4, and 6 h 94 had reduced the dimension 1,078, 475, 398, 357, and 203, respectively. The size reduction closely coincided with the increase in the surface area of 41, 55, 72, 83, and 110 m^2. Such phenomenal increase in the surface area provides extensive surface area for nutrient adsorption and desorption. The status of nano-fertilizer research has recently reviewed by Subramanian *et. al.* (2015).

Nano-fertilizer is known to release nutrients for a longer period of time particularly N which has an added advantage of environmental protection. Nitrogen management is one of the potential strategies to minimize the greenhouse gas (GHG) emission from wetlands. Recently, Rajkishore *et. al.* (2015) have demonstrated that split application of N in two systems of rice cultivation namely Conventional and system of rice intensification (SRI) found to minimize the methane emission from wet lands which is closely

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associated with the increased activities of methanogens in the rice soils. The published literatures on slow release N fertilizers or split application of N fertilizer can slow down the release of N which can help to improve the N use efficiency and minimize the environmental hazard. With this in view, the research was attempted to introduce an innovative forms of nano-fertilizer carrying (NO_3^- & NH_4^+) in rice soils and to examine the N dynamics and GHG emission.

2. MATERIALS & METHODS

2.1. Synthesis of zeolite based nano-fertilizer carrying nitrate and ammonical forms of nitrogen

The zeolite (Zinghal chemicals Pvt Ltd, Gujarat, India) was purchased from M/s Singhal Chemicals, Ahmadabad, Gujarat, was used for this study. Two forms of N namely NO_3^- and NH_4^+ forms were fortified in the zeolite substrate. Zeolite is an alumino-silicate mineral possessing negative charge on its surface which had to be surface modified partially to positive charge to enable fortification of nitrate ions on the adsorptive sites. A surfactant hexadecyltrimethylammoniumbromide (HDTMABr from Sigma Aldrich, Bangalore) was used for surface modification of nano-zeolite (Bansiwal, 2006). A pre-weighed quantity of nano-zeolite was mixed with HDTMABr solution in a 1:100 solid:liquid ratio. The solution was mixed in a ultracentrifuge at 150 rpm for 7-8 hrs. Thereafter, the mixture was centrifuged at 5000 rpm for 20 minutes. The supernatant was tested for the retention of the surfactant on the adsorptive sites using HPLC. The solid portion of nano-zeolite after treated with HDTMABr solution was dried for two weeks and surface modification of nano-zeolite was confirmed by Zeta Analyzer, Fourier Transform Infrared Spectroscopy (FTIR) and Energy Dispersive X-ray Spectroscopy (EDAX). The surface-modified zeolite washed with double distilled water and air dried for 4-6 hrs. Synthesized surface-modified zeolite was mechanically ground using pestle and mortar to achieve fine particles. In a 40-ml centrifuge tube, 2.5g of surface modified zeolite was added with 25 ml of varying concentrations of potassium nitrate solution (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 M) and mixed well for 24 h at 150 rpm (Li, 2003). The residue was shade-dried and used as a nitrate fertilizer. Similar procedure was adopted for loading of NH_4^+ without surface modification in the zeolite.

2.2 Characterization of nano-fertilizer

The nano-fertilizer carrying NO_3^- and NH_4^+ forms were characterized before and after loading of nutrients. Size of the particles was determined using particle size analyzer (HORIBA-SZ-100, Japan). The stability of the nano-fertilizer was assessed by zeta analyzer. The shape was examined in a Scanning Electron Microscope (FEI, Quanta 200, Netherlands) was used to get the shape of the nano-zeolite. About 0.5 to 1.0 g of nano-zeolite sample was dusted on the carbon conducting tape. Then the tape was mounted on sample stage and the images were taken in 17,000 magnification and 12.50KV. The X-ray Diffraction technique was used for Crysatlline measurement . The Fourier Transform Infrared Spectroscopy (FTIR) technique was employed to confirm the loading of nitrogen. The nitrogen loading in nano-zeolite was quantified using FEI QUANTA 250 EDAX.

2.3. Sorption and desorption of nitrogen from nano-zeolite

To study the sorption behaviour of nitrate form (potassium nitrate) of surface modified nano-zeolite and ammoniacal (ammonium sulphate) form of nano-zeolite, to each 40-ml centrifuge tube, 2.5g of surface modified zeolite and unmodified nano-zeolite and 25 ml of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 & 4.0 M ammonium sulphate and potassium nitrate solution were mixed for 24 h at 150 rpm (Li, 2003). The mixtures were then centrifuged and the solution was filtered and nitrate and ammonical nitrogen concentrations were determined by Kjeldahl distillation. The amount of nitrate and ammonical forms of nitrogen was calculated from the difference between the initial and equilibrium solution concentrations (Jackson, 1958).

2.4. Determination of nitrate-nitrogen and ammonical-nitrogen

About 250 ml of filtered solution was pipetted into the distillation flask and 500ml of distilled water was added. In a 250ml beaker, 25 ml of N/10 H_2SO_4 with one or two drops of methyl red indicator was added and kept at the delivery end of the distillation set. A spoon of magnesium oxide (5g) was added to release ammonia. The evolved ammonia was collected in the standard acid. When the distillate ran free of ammonia, the tumbler was removed from the delivery end and titrated against N/10 KOH and the nitrate nitrogen content was calculated from the titre value. Then 3 g of Devarda's alloy, glass beads and about 10 ml of 40 % NaOH was added to the distillation flask and the distillation flask was closed and allowed the reaction to proceed. The evolved ammonia was collected in the standard acid. When the distillate ran free of ammonia, the tumbler was removed from the delivery end and titrated against N/10 KOH and nitrate and ammonical form of nitrogen contents were calculated (Jackson, 1958).

2.5 Percolation reactor study

The chemical reactor designed for a constant flow of solution in several studies concerning zeolites was used (Sharmila Rahale, 2011). By this

technique, nutrient retention and release characteristics can be determined. The chemical reactor consists of a Teflon cylinder (internal diameter= 2.5 cm, height = 15 cm) through the top of which deionized water is continuously pumped at a flow rate of 66 ml per day. Inside the reactor, 5 g of soil overlaid with the fertilizer were placed. Solutions were collected to determine ammonium and nitrate ions. The mean temperature during the experiment was 25 ± 0.2°C.

2.6 Greenhouse Experiment

A greenhouse study was conducted at Agro-Climate Research Centre (ACRC), Tamil Nadu Agricultural University, Coimbatore. Rice (var. white ponni) seedlings were transplanted in tubs (length x width x height (1.4m x 0.8m x 0.5m). The tubs were divided by 30 cm deep plastic plates to create 6 sub-plots (70cm x 25 cm). Each sub-plot had nine plants. The tubs were filled with 750 Kg of wetland soil and irrigated with water up to a depth of 2.5 cm. A recommended dose of 50:50 kg PK ha^{-1} was applied to the crop uniformly to all the treatments .The entire dose of P (31.3 g / 250 kg of soil) in the form of single super phosphate (16 per cent P_2O_5) was applied as basal application. Potassium in the form of muriate of potash (60 per cent K_2O) was applied in four equal splits. Nitrogen was applied as per treatment in the form of urea (46% N), zeolite-based NO_3-N (6.2% N) or zeolite-based NH_4^+ - N (12.6% N). Each sub-plot was fertilized accordingly to the N content of the fertilizer formulation.

2.7 Statistical Analysis

The data collected from various experiments were analysed using analysis of variance (ANOVA).

3. RESULTS & DISCUSSION

3.1. Characterization of nano-zeolite

The characteristics of nano-zeolite before and after loading N is presented (Table 1). The size of the nano-zeolite was measured in a particle size analyzer and the size varied from 7-15 nm with an average dimension of 7.6 nm. The distribution of the particle suggested that more than 90% of the particles are in nano- dimension and appears to be homogeneous. The zeta potential of nano-zeolite was -42 mV and on surface modification, the surface charge changed to +1 mV at 67 mM concentration of hexadecyltrimethyl ammonium bromide (HDTMABr) surfactant. The data are in agreement with the reports of Subramanian and Sharmila Rahale (2009).

The shape of the nano-zeolite was cubical in shape before loading N and turned irregular after loading N in nano-zeolite as exhibited by the images of SEM (Fig. 1a-d). The changes in shape indicate the adsorption of N on the sheet of zeolite. The CEC of the nano-zeolite was 270 (c mol (p^+) kg^{-1}) which reduced to 220 (c mol (p^+) kg^{-1}) after it becomes nano-fertilizer. The reduction in CEC is attributed to the space occupied by either NO_3^- or NH_4^+. The SiO_2/Al_2O_3 molar ratio of nano-zeolite recorded the highest ratio of 2.0 whereas the nitrogen loaded nano-zeolite was 1.83 (Table-1).

The loading of both NH_4^+ - N and NO3-N in nano-zeolite and surface modified nano-zeolite (SMNZ), respectively, were confirmed by FT-IR (Fig. 2a-d). The FTIR spectra of nano-zeolite loaded with NH_4^+– N showed characteristic peaks at wave numbers 3695.61, 2854.65, 2924.09, 1442.75, 752 and 551 cm^{-1}. besides the peaks at 1870.95 and 2519.03 cm^{-1} in NH_4^+–N loaded nano-zeolite can be assigned to ammoniacal form of nitrogen sorbed on the nano-zeolite surface as corresponding peaks that are also observed in the IR pattern of nitrogen only (peaks at 790.81, 729.09 and 1816.94 cm^{-1}). The IR pattern of SMNZ loaded with NO_3^-–N showed characteristic peaks at wave numbers 3691.75, 3630.03, 2519.03, 1870.95, 999.13 and 424.34 cm^{-1}.besides the peaks at 1870.95 and 1809.23 cm^{-1} in NO_3^-–N loaded SMNZ can be assigned to nitrate form of nitrogen sorbed on the SMNZ surface as the corresponding peaks that are also observed in the IR pattern of nitrogen only (peaks at 3016.67, 3471.87 and 837.11 cm^{-1}). The data are in conformity with the reports of Manikandan and Subramanian (2014).

The EDAX (Energy dispersive X-ray spectroscopy) data further confirmed the adsorption of NH_4^+–N, NO_3^-–N on the nano-zeolite (Fig 3a-3d). Mineral composition of pure zeolite consists of carbon (11.74%), oxygen (44.79%), magnesium (8.18%), aluminium (4.66%), silica (26.19%) and calcium (4.43%).The result showed that NH_4^+–N loaded zeolite in addition to these minerals the nitrogen (10.2) was also included in the mineral composition. The NO_3^-–N loaded zeolite showed these minerals and in addition nitrogen (7.2%) was adsorbed by the surface modified nano-zeolite.

The XRD pattern of nano-zeolite before and after loading NH_4^+–N peaks at 2θ =17.23, 25.50, 31.10, 39.11, 45.12, 55.15 and 70.01 was observed for pure nano-zeolite (Fig 4a- 4d). When it was loaded NH_4^+-N, there was a change in peaks (2θ = 12.88, 29.01, 45.11, 50.11, 75.02, 80.19, 80.77) .These peaks clearly showed that NH_4^+–$N^-$was attached on nano-zeolite.NO_3^--N, there was change in peaks (2θ = 10.72, 21.05, 29.71, 43.57, 49.76, 56.73, 76.59, 85.19).These peaks clearly showed that NO_3^-- N was attached on surface modified nano-zeolite.

3.2 Greenhouse gas (GHG) emission

The nitrous oxide emission was measured at 30 and 60 DAT in rice soils being exposed to various

fertilization treatments. During the active tillering, plots applied with NH_4^+–N loaded nano-zeolite showed the lowest N_2O emission of 0.88 mg m^{-2} day^{-1} while the conventional fertilization practice registered the highest value (1.67 mg m^{-2} day^{-1}) which is nearly twice as that of treated plots (Fig-5). Similar trend of response was seen at 60 DAT.

The CH_4 emission was measured at 30 and 60 DAT in rice soils being exposed to various fertilization treatments (Fig-6). During the active tillering, plots applied with NO_3–N loaded nano-zeolite showed the lowest CH_4 emission of 13.6 mg m^{-2} day^{-1} while the conventional fertilization practice registered the highest value (14.5 mg m^{-2} day^{-1}) which is significantly higher than that of treated plots but comparable to NH_4^+–N loaded nano-zeolite fertilized plots. Similar trend of response was seen at 60 DAT.

4. CONCLUSION

Nano-fertilizer (nitrogen) synthesized using zeolite is found to release N slowly and steadily to an extended period of time up to 10-12 days. As a result of slow release of N, the microbial activities get slowed down accordingly which eventually resulted in reduction of potential greenhouse gas emission such as nitrous oxide and methane in rice fields. This study clearly suggested that nano-fertilizer technology is a potential strategy to minimize the greenhouse gas emission in rice fields and lessened the illeffects associated with global warming.

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